

PATENT ABSTRACTS OF JAPAN

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(21) Application number : 03-030206 (71) Applicant : NIPPON STEEL CORP
(22) Date of filing : 25. 02. 1991 (72) Inventor : TANIMURA KOJI
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(54) PRODUCTION OF ZN-NI ALLOY ELECTROPLATED STEEL SHEET EXCELLENT IN WORKABILITY

(57) Abstract:

PURPOSE: To improve the corrosion resistance and press workability of a steel by plating it at prescribed current in a Zn-Ni alloy plating bath contg. a trace of Sb and controlling the shape of the crystals of the plating.

CONSTITUTION: A Zn-Ni alloy plating soln. contg. 0.5 to 5ppm Sb is prep'd., e.g. by adding antimony oxide to an acidic soln. contg. sulfuric acid. In this plating soln., the steel sheet is electroplated at 10 to 150A/dm² current density to obtain rice-granular plating crystals, e.g. having 1 to 3 μm minor axis and 2 to 5 μm major axis. The Zn-Ni alloy plating constituted of the same crystals is good in the retentibity of lubricating oil at the time of press working and is excellent in press workability.

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L1 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1994:538653 CAPLUS
DN 121:138653
ED Entered STN: 17 Sep 1994
TI Manufacture of steel sheets electroplated with Zn-Ni alloys with excellent
formability
IN Tanimura, Koji; Yamazaki, Fumio; Shindo, Yoshio
PA Nippon Steel Corp, Japan
SO Jpn. Kokai Tokkyo Koho, 6 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
IC ICM C25D005-26
CC 55-6 (Ferrous Metals and Alloys)
Section cross-reference(s): 56, 72

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 06116781	A	19940426	JP 1991-30206	19910225 <--
	JP 07103476	B	19951108		
PRAI	JP 1991-30206		19910225		

CLASS

	PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
	JP 06116781	ICM	C25D005-26
		IPCI	C25D005-26 [ICM,5]
AB	In electroplating of Zn-Ni alloys on steel sheets to give the title sheets, the baths contain 0.5-5 ppm of Sb, and the electroplating is carried out by c.d. 10-150 A/dm ² . The sheets have high press formability.		
ST	steel electroplating zinc nickel alloy		
IT	Electrodeposition and Electroplating (of zinc-nickel alloys, on steels, for formability)		
IT	1309-64-4, Antimony oxide (Sb ₂ O ₃), uses 7440-36-0, Antimony, uses RL: USES (Uses) (baths containing, electroplating, for zinc-nickel alloy coatings on steels)		
IT	52360-06-2P 58923-87-8P 77025-17-3P 84697-76-7P 87436-31-5P 87557-20-8P 108690-50-2P RL: PREP (Preparation) (coatings, on steels, electroplating for formation of)		
IT	12597-69-2, Steel, uses RL: PEP (Physical, engineering or chemical process); PROC (Process) (electroplating of, with zinc-nickel alloys, with high formability)		

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XP-002340830

(C) WPI / DERWENT

AN - 1994-174186 [49]

AP - JP19910030206 19910225; JP19910030206 19910225; [Based on J06116781]

CPY - YAWA

DC - M14

FS - CPI

IC - C25D3/56 ; C25D5/26

MC - M11-A04

PA - (YAWA) NIPPON STEEL CORP

PN - JP6116781 A 19940426 DW199421 C25D5/26 006pp

- JP7103476B B2 19951108 DW199549 C25D5/26 005pp

PR - JP19910030206 19910225

XA - C1994-079905

XIC - C25D-003/56 ; C25D-005/26

AB - J06116781 Prodn. comprises adding 0.5-5 ppm Sb into a Zn-Ni coating bath and applying 10-150 A/dm².

- USE/ADVANTAGE - Used for automobiles and household electric appliances, due to the improved press-formability while maintaining the high corrosion resistance.

- In an example, to a cold rolled steel sheet (0.8 mm thick) was applied a Zn-Ni coating at a coating wt of 30 g/m in a bath of sulphuric acid with addn. of Sb (as Sb₂O₃) at a rate of 2 ppm. The press formability (and corrosion resistance (SST test) showed satisfactory results.(Dwg.0/0)

IW - PRODUCE ZINC@ NICKEL@ ALLOY ELECTROCOATING STEEL SHEET COMPRIZE ADD ANTIMONY@ COATING BATH APPLY CURRENT AUTOMOBILE

IKW - PRODUCE ZINC@ NICKEL@ ALLOY ELECTROCOATING STEEL SHEET COMPRIZE ADD ANTIMONY@ COATING BATH APPLY CURRENT AUTOMOBILE

NC - 001

OPD - 1991-02-25

ORD - 1994-04-26

PAW - (YAWA) NIPPON STEEL CORP

TI - Prodn of zinc@ nickel@ alloy electrocoating steel sheet - comprising adding antimony@ into coating bath and applying current, used for automobiles

(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

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技術表示箇所

審査請求 有 請求項の数1(全6頁)

(21)出願番号 特願平3-30206

(22)出願日 平成3年(1991)2月25日

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(54)【発明の名称】 加工性に優れたZn-Ni系合金電気めっき鋼板の製造方法

(57)【要約】

【目的】 本発明はZn-Ni系合金めっきの結晶形態をコントロールすることにより、加工性に優れた自動車、家電用途に好適なZn-Ni系合金めっき鋼板の製造方法を提供するものである。

【構成】 Zn-Ni系合金電気めっき鋼板の製造に際して、Zn-Ni系合金めっき浴中にSbを0.5~5ppm含有させて、電流密度1~150A/dm²で鋼板に電気めっきを行なうことを特徴とする加工性に優れたZn-Ni系合金電気めっき鋼板の製造方法。

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【特許請求の範囲】

【請求項1】 $Zn-Ni$ 系合金電気めっき鋼板の製造に際して、 $Zn-Ni$ 系合金めっき浴中に Sb を $0.5 \sim 5 \text{ ppm}$ 含有させて、電流密度 $10 \sim 150 \text{ A/dm}^2$ で鋼板に電気めっきを行なうことを特徴とする加工性に優れた $Zn-Ni$ 系合金電気めっき鋼板の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は優れた加工性を有し、自動車や家電用として好適な $Zn-Ni$ 系合金電気めっき鋼板の製造方法に関する。

【0002】

【従来の技術】 冷延鋼板の耐食性や塗装後耐食性を向上させ、加工性を損なわずに量産できる表面処理鋼板として電気亜鉛めっき鋼板が汎用されていることは周知である。近年では寒冷地帯における冬期の道路凍結防止用の散布岩塩に対する自動車の防錆対策として亜鉛めっき鋼板の使用が試みられ、苛酷な腐食環境での高度な耐食性が要求されている。亜鉛めっき鋼板の耐食性の向上要求に対しては、亜鉛のめっき量（付着量）の増加という手段があるが、これは溶接性や加工性の点で問題が多い。そこで亜鉛自身の溶解を抑制し亜鉛めっきの寿命を延ばす方法として、多くの合金めっきが提案されている。これらの多くは Fe , Co , Ni といった鉄族金属を合金成分として含有する Zn 系合金めっきである。

【0003】 この内、 $Zn-Ni$ 系合金めっき鋼板は、特に未塗装耐食性に優れ、塗装後性能や加工性、溶接性も良好なことから、自動車用防錆鋼板を始めとして広く使用されている。しかしながら、要求品質の全てを十分に満たすものではないことから、例えば特開平2-70089号公報では化成処理性に優れた Zn 系合金めっきの製造方法、特開平2-70091号公報では耐衝撃密着性に優れた $Zn-Ni$ 合金めっき鋼板など、特定の性能を向上させるための種々の技術が開示されている。最近の動向として、自動車、家電用途を中心に高度のプレス加工性が要求されつつあり、より加工性に優れた $Zn-Ni$ 系合金めっき鋼板が望まれている。これに対しては、鋼板材質による対応はもとより高度のプレス加工に耐えうる潤滑油の検討も行なわれているが、 $Zn-Ni$ 系合金めっきそのものの加工性を向上させうるものではないため、本質的な解決には到っていない。

【0004】

【発明が解決しようとする課題】 $Zn-Ni$ 系合金めっき鋼板に対する高度のプレス加工性要求を満たすためには、鋼板材質やプレス加工性に使用する潤滑油の検討だけでなく、 $Zn-Ni$ 系合金めっきそのものにプレス加工性の向上機能を付与する必要がある。 $Zn-Ni$ 系合金めっきは、 $Zn-Ni$ の合金相である γ 相が形成される Ni 含有率において高度の耐食性を発揮することは公知である。しかし、高耐食性が発現される Ni 含有率範

囲におけるめっきの結晶形態は緻密で粗度が小さく、プレス加工時の潤滑油保持力が乏しいため、プレス加工に適したものではない。そこで、本発明者らは、 $Zn-Ni$ 系合金めっきの結晶を潤滑油保持力の高い形態にコントロールすることができれば、プレス加工性は向上すると推定し、結晶形態の制御方法について観察検討した結果、本発明に到った。

【0005】

【課題を解決するための手段】 本発明の要旨は、 $Zn-Ni$ 系合金電気めっき鋼板の製造に際して、 $Zn-Ni$ 系合金めっき浴中に Sb を $0.5 \sim 5 \text{ ppm}$ 含有させて、電流密度 $10 \sim 150 \text{ A/dm}^2$ で鋼板に電気めっきを行なうことを特徴とする加工性に優れた $Zn-Ni$ 系合金電気めっき鋼板の製造方法である。

【0006】

【作用】 本発明の特徴は、 $Zn-Ni$ 系合金めっき浴に極微量の Sb (アンチモン) を含有させて電気めっきを行なう点である。 $Zn-Ni$ 系合金めっき鋼板の耐食性は Ni 含有率に支配され、 $\gamma Zn-Ni$ 相が形成され、 αNi 相が形成されない範囲、すなわち Ni 含有率 $5 \sim 20\%$ で高耐食性を発揮し、 $10 \sim 15\%$ の γ 単相領域においては特に優れた耐食性を発揮する。 γ 相のめっき結晶は緻密で粗度が小さいので、プレス加工時に潤滑油を十分に保持できず、これが厳しいプレス加工性の阻害要因になっている。ところが、 $Zn-Ni$ 系合金めっき浴の中に Sb を極微量添加し、適当な条件で電解することにより、短径が $1 \sim 3 \mu$ 、長径が $2 \sim 5 \mu$ の米粒状のめっき結晶が得られる。

【0007】 かかる米粒状結晶のめっき結晶である $Zn-Ni$ 系合金めっきは、プレス加工時の潤滑油保持性が良好であるため、緻密で低粗度の従来の $Zn-Ni$ 系合金めっきに比較してプレス加工性が格段に優れる。例えば、絞り加工時に要する荷重を $1 \sim 3$ 割低減させることができる。結晶形態の変化に伴ない耐食性の劣化が懸念されるところであるが、 Ni 含有率を耐食性良好域に制御しておけば耐食性劣化については、無視しうるレベルである。 Sb の添加量は、 $0.5 \sim 5 \text{ ppm}$ が適当であり、 0.5 ppm 未満では結晶形態への影響が顕著でなく、 5 ppm を超えると耐食性劣化が無視できなくなるので、好ましくない。より好ましい Sb の添加量範囲は、 $1 \sim 3 \text{ ppm}$ である。

【0008】 Sb を添加しためっき浴から、上記の $Zn-Ni$ 系合金めっきを得るためにには、さらに電流密度 $10 \sim 150 \text{ A/dm}^2$ とする必要がある。 Sb は電解時に陰極である鋼板面に吸着して $Zn-Ni$ の電析に影響を及ぼすものと推定されるが、極微量であるため、高電流密度では拡散律速となり、 $Zn-Ni$ の電析に追随できなくなる、したがって結晶形態への作用が低下する。このような理由から、電流密度の上限は 150 A/dm^2 とする。また生産効率の面から、 10 A/dm^2 以下の低電

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流密度は好ましくない。

【0009】本発明で対象とするZn-Ni系合金めっきとは、主としてNiを含有するZnめっきであり、具体的にはZn-Ni、あるいはZn-Ni-Co, Zn-Ni-Fe, Zn-Ni-Cr, Zn-Ni-Fe-CrなどZn-Niに他の金属成分を含有するものを目指す。Ni含有率は5~20重量%が好ましい。5重量%未満では耐食性が不足し、20重量%を超えると加工性が劣化するので好ましくない。より好ましい範囲は10~15重量%である。Ni以外の金属成分は、総量で5重量%未満が好ましく、5重量%以上ではNiの効果が減殺されるので好ましくない。付着量については10~50g/m²が好ましい。

【0010】めっき浴に関して、金属イオン濃度、pH、浴温などについては特に制約はなく、例えばZn²⁺, Ni²⁺イオンを全濃度で0.5~2.5モル/1、pH 0.5~6、浴温 40~70℃の硫酸酸性浴、もしくは塩化物浴を用いることができるが、不溶性電極を用いることができる硫酸酸性浴の使用が有利である。めっき浴中には、必要に応じてFe²⁺, Co²⁺, Cr³⁺イオンなどを少量含有させてもよく、電導度を高めるために、Na⁺, NH₄⁺, K⁺, Mg²⁺イオンなどの無関係塩を添加してもよい。液流速については、Sbの効果を鋼板上に均一に発揮するために、10~2000m/minとすることが好ましい。

【0011】

【実施例】板厚0.8mmの冷延鋼板（深絞り用低炭素鋼板）を、アルカリ脱脂し、5%硫酸水溶液で酸洗した後、種々のめっき条件で付着量30g/m²のZn-Ni系合金めっきを行なった。めっき浴としては硫酸酸性浴を用い、Sbは酸化アンチモン（Sb:O₃）として添加した。こうして得られたZn-Ni系合金めっき鋼板のめっき組成を調べ、プレス加工性と耐食性を評価した。これらをまとめて表1に示した。プレス加工性と耐

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食性の評価方法を以下に示す。

(1) プレス加工性

円筒深絞り試験（絞り比2.0、しづ押さえ0.5ton, 絞り速度25mm/分）を行なったときの最大ポンチ荷重で評価した。潤滑油としては出光興産（株）製Z-3を用い、これをZn-Ni系合金めっき鋼板の表面に1g/m²塗布した。

最大ポンチ荷重4ton 未満 : ○

4~4.5ton : ○

4.5ton超 : ×

(2) 耐食性

めっきのまま塩水噴霧試験（JIS Z 2371）を36時間行なった時の赤錆発生面積で評価した。

赤錆発生面積1%未満 : ○

1~5% : ○

5%超 : ×

表1において、本発明例1~5は比較例1, 2, 3と対比される。本発明例1~5は、めっき浴中にSbが添加されていない比較例1と比べて、プレス加工性が良好であり、耐食性も同等である。

【0012】しかし、比較例2のようにめっき浴中のSbが多すぎると、耐食性は低下する。また、比較例3のように、めっき浴中に適当量のSbが添加されていても電流密度が高すぎると、プレス加工性に効果がない。本発明例6~8は比較例4と、本発明例9~11は比較例5とそれぞれ対比され、本発明例は、めっき浴中にSbが添加されていない比較例に比べてプレス加工性が良好であり、耐食性も同等である。少量のCo, Fe, Crを含む本発明例15~17と他の本発明例も、Sb添加によるプレス加工性の向上効果は明らかであり、耐食性の低下も認められない。

【0013】

【表1】

表1-1

区分	No.	めつき浴組成				pH	浴温(℃)
		Zn ²⁺ (g/l)	Ni ²⁺ (g/l)	Sb (ppm)	その他(g/l)		
本発明例	1	35	45	2		Na ⁺ 32	2 60
	2	35	45	1		Na ⁺ 32	1 60
	3	35	45	5		Na ⁺ 32	1.5 60
	4	35	45	3		Na ⁺ 32	3 60
	5	35	45	0.5		Na ⁺ 32	1.8 60
	6	30	30	3		NH ₄ ⁺ 14	2 60
	7	30	30	0.5		NH ₄ ⁺ 14	1.8 60
	8	30	30	1		NH ₄ ⁺ 14	1.5 60
	9	40	55	0.5		K ⁺ 22	2 50
	10	40	55	2		K ⁺ 22	1.8 50
	11	40	55	1		K ⁺ 22	1.5 50
	12	45	60	2		Mg ²⁺ 10	2 50
	13	20	15	1		Mg ²⁺ 10	1.8 50
	14	60	80	1		Mg ²⁺ 10	1.5 50
	15	35	45	2	Co ²⁺ 10	Na ⁺ 16	2 60
	16	35	45	2	Fe ²⁺ 10	Na ⁺ 16	1.8 60
	17	35	45	2	Cr ³⁺ 5	Na ⁺ 16	1.5 60
比較例	1	35	40	-		Na ⁺ 32	2 60
	2	35	40	7		Na ⁺ 32	1.5 60
	3	35	40	1		Na ⁺ 32	1 60
	4	30	25	-		NH ₄ ⁺ 14	2 50
	5	40	50	-		K ⁺ 22	2 50

[0014]

[表2]

表1-2

区分	No	電流速度 (N/dm ²)	液流速 (m/min)	めっき組成		プレス 加工性	耐食性
				Ni (重量%)	その他 (重量%)		
本発明例	1	70	90	12		◎	◎
	2	150	90	11		○	◎
	3	50	90	10		◎	○
	4	10	90	13		◎	◎
	5	30	90	10		○	◎
	6	30	60	9		◎	○
	7	70	60	8		○	○
	8	100	60	9		◎	◎
	9	30	30	13		○	◎
	10	70	30	11		◎	◎
	11	100	30	12		◎	◎
	12	30	120	13		◎	◎
	13	70	120	10		◎	◎
	14	100	120	15		○	○
	15	30	90	12	Co 0.5	◎	◎
比較例	16	70	90	11	Fe 1	◎	◎
	17	100	90	12	Cr 0.1	◎	◎
	1	70	90	12		×	◎
	2	50	90	10		◎	×
	3	200	90	11		×	◎
	4	30	60	9		×	◎
	5	30	30	13		×	◎

【0015】

【発明の効果】本発明のZn-Ni系合金電気めっき鋼板の製造方法によれば、Zn-Ni系合金めっき本来の高耐食性を維持しつつ、プレス加工性を向上させること

が可能であり、高度のプレス加工性を要求される自動車、家電用途に好適なZn-Ni系合金電気めっき鋼板を提供することができる。

【手続補正書】

【提出日】平成3年5月30日

【補正内容】

【手続補正1】

【0014】

【補正対象書類名】明細書

【表2】

【補正対象項目名】0014

【補正方法】変更

表1-2

区分	No	電流速度 (A/dm ²)	液流速 (m/min)	めっき組成		プレス 加工性	耐食性
				Ni (重量%)	その他 (重量%)		
本発明例	1	70	90	12		◎	◎
	2	150	90	11		○	◎
	3	50	90	10		◎	○
	4	10	90	13		◎	◎
	5	30	90	10		○	◎
	6	30	60	9		◎	○
	7	70	60	8		○	○
	8	100	60	9		◎	◎
	9	30	30	13		○	◎
	10	70	30	11		◎	◎
	11	100	30	12		◎	◎
	12	30	120	13		◎	◎
	13	70	120	10		◎	◎
	14	100	120	15		○	○
	15	30	90	12	Co 0.5	◎	◎
	16	70	90	11	Fe 1	◎	◎
	17	100	90	12	Cr 0.1	◎	◎
比較例	1	70	90	12		×	◎
	2	50	90	10		◎	×
	3	200	90	11		×	◎
	4	30	60	9		×	◎
	5	30	30	13		×	◎

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention has the outstanding workability and relates to the manufacture approach of an automobile or a Zn-nickel system alloy electroplating steel plate suitable as an object for household electric appliances.

[0002]

[Description of the Prior Art] It is common knowledge that the electrolytic zinc-coated carbon steel sheet is used widely as a surface treated steel sheet which can be mass-produced without raising the corrosion resistance of cold rolled sheet steel and the corrosion resistance after paint, and spoiling workability. The activity of a galvanized steel sheet is tried as a cure against rust proofing of the automobile to the spraying rock salt for the route anti-freeze of the winter in a cold district band, and recent years require the advanced corrosion resistance in cruel corrosive environment. Although there is a means of the increment in the zincy amount of plating (coating weight) to the corrosion resistance improvement demand of a galvanized steel sheet, this has many problems in respect of weldability or workability. Then, many alloy platings are proposed as an approach of controlling the dissolution of zinc itself and prolonging the life of a galvanization. These many are Zn system alloy platings which contain iron-group metals, such as Fe, Co, and nickel, as an alloy content.

[0003] Among this, especially a Zn-nickel system alloy-plating steel plate is excellent in non-painted corrosion resistance, and since the engine performance after paint, and workability and weldability are also good, the rust-proofing steel plate for automobiles is widely used as the start. However, by the manufacture approach of Zn system alloy plating excellent in chemical conversion nature, and JP,2-70091,A, various techniques for raising the specific engine performance, such as a Zn-nickel alloy-plating steel plate excellent in shock-resistant adhesion, are indicated at JP,2-70089,A from it not being what fully fulfills all the demand quality, for example. As latest trend, advanced press-working-of-sheet-metal nature is being required focusing on an automobile and a household-electric-appliances application, and a Zn-nickel system alloy-plating steel plate which was more excellent in workability is desired. Although examination of the lubricating oil which can be equal to the response by steel plate construction material to this at press working of sheet metal advanced from the first is also performed, since it is not that in which the workability of the Zn-nickel system alloy plating itself is raised, and it deals, it has not resulted in essential solution.

[0004]

[Problem(s) to be Solved by the Invention] In order to fill the advanced press-working-of-sheet-metal nature demand to a Zn-nickel system alloy-plating steel plate, it is necessary to give the improvement function of press-working-of-sheet-metal nature to not only examination of the lubricating oil used for steel plate construction material or press-working-of-sheet-metal nature but the Zn-nickel system alloy plating itself. The Zn-nickel system alloy plating of demonstrating advanced corrosion resistance in nickel content in which gamma-phase [which is an alloy phase of Zn-nickel] is formed is well-known. However, the crystalline form of the plating in nickel content range in which high corrosion resistance is

discovered is precise, is small, and since the lubricating oil holding power at the time of press working of sheet metal is scarce, it is not a thing suitable for press working of sheet metal. [of relative roughness] Then, when this invention persons could control the crystal of a Zn-nickel system alloy plating in the high gestalt of lubricating oil holding power, as a result of presuming that press-working-of-sheet-metal nature improves and considering the control approach of a crystalline form wholeheartedly, it resulted in this invention.

[0005]

[Means for Solving the Problem] Manufacture of a Zn-nickel system alloy electroplating steel plate is faced, and the summary of this invention is 0.5-5 ppm about Sb during a Zn-nickel system alloy-plating bath. It is made to contain and they are current density 10 - 150 A/dm². It is the manufacture approach of a Zn-nickel system alloy electroplating steel plate excellent in the workability characterized by electroplating to a steel plate.

[0006]

[Function] The description of this invention is a point which electroplates by making a Zn-nickel system alloy-plating bath contain Sb (antimony) of ultralow volume. The corrosion resistance of a Zn-nickel system alloy-plating steel plate demonstrates the corrosion resistance which demonstrated high corrosion resistance and was excellent in the range of 5 - 20% in which nickel content rules over, gammaZn-nickel phase is formed in, and alphanickel phase is not formed, i.e., nickel content, especially in 10 - 15% of gamma single phase field. Since a gamma-phase plating crystal is precise and relative roughness is small, a lubricating oil cannot fully be held at the time of press working of sheet metal, but this has become the inhibition factor of severe press-working-of-sheet-metal nature. However, the plating crystal of the shape of a grain of rice 1-3micro, and whose major axis a minor axis is 2-5micro is obtained by carrying out ultralow volume addition of the Sb, and electrolyzing on suitable conditions into a Zn-nickel system alloy-plating bath.

[0007] since the lubricating oil holdout at the time of press working of sheet metal is good, the Zn-nickel system alloy plating which becomes as the plating crystal of this grain-of-rice-like crystal is precise, and as compared with the conventional Zn-nickel system alloy plating of low relative roughness, press-working-of-sheet-metal nature boils it markedly, and is excellent. For example, the load required at the time of spinning can be reduced 1 to 30 percent. Although it is just going to be anxious about corrosion resistance degradation with change of a crystalline form, if nickel content is controlled in the corrosion-resistant good region, it will be the level which can be disregarded about corrosion-resistant degradation. The addition of Sb is 0.5-5 ppm. It is suitable and is 0.5 ppm. In the following, the effect on a crystalline form is not remarkable, and it is 5 ppm. Since it becomes impossible to disregard corrosion-resistant degradation when it exceeds, it is not desirable. the more desirable addition range of Sb -- 1-3 ppm it is .

[0008] In order to obtain the above-mentioned Zn-nickel system alloy plating from the plating bath which added Sb, they are current density 10 - 150 A/dm² further. It is necessary to carry out. Although Sb is presumed to be what sticks to the steel plate side which is cathode, and affects the electrocrystallization of Zn-nickel at the time of electrolysis, since it is ultralow volume, with high current density, become a diffusion limitation, it becomes impossible to follow in footsteps of electrocrystallization of Zn-nickel therefore, and the operation to a crystalline form falls. The upper limits of current density since it is such are 150 A/dm². It carries out. Moreover, the field of productive efficiency to 10 A/dm² The following low current consistencies are not desirable.

[0009] The target Zn-nickel system alloy plating is Zn plating which mainly contains nickel in this invention, and what specifically contains other metal components in Zn-nickel, such as Zn-nickel or Zn-nickel-Co, Zn-nickel-Fe, Zn-nickel-Cr, and Zn-nickel-Fe-Cr, is pointed out. nickel content has 5 - 20 desirable % of the weight. At less than 5 % of the weight, since workability will deteriorate if corrosion resistance runs short and it exceeds 20 % of the weight, it is not desirable. The more desirable range is 10 - 15 % of the weight. Metal components other than nickel have less than 5 desirable % of the weight in a total amount, and at 5 % of the weight or more, since the effectiveness of nickel is reduced, they are not desirable. About coating weight, 10 - 50 g/m² is desirable.

[0010] Although there is especially no constraint about metal ion concentration, pH, and bath temperature, for example, 0.5-2.5 mols [1.] /, pH 0.5-6, the sulfuric-acid acidity bath of 40-70 degrees C of bath temperature, or a chloride bath can be used for Zn²⁺ and nickel²⁺ ion by total concentration about a plating bath, the activity of the sulfuric-acid acidity bath which can use an insoluble anode is advantageous. In order to carry out little content of Fe²⁺, Co²⁺, the Cr³⁺ ion, etc. if needed and to raise electric conductivity during a plating bath, indifferent salt, such as Na⁺, NH⁴⁺, K⁺, and Mg²⁺ ion, may be added. In order to make homogeneity demonstrate the effectiveness of Sb on a steel plate about the liquid rate of flow, it is 10 - 200 m/min. Carrying out is desirable.

[0011]

[Example] It is coating weight 30 g/m² at the various plating conditions after it carries out alkaline degreasing of the cold rolled sheet steel (low-carbon steel plate for deep drawing) of 0.8mm of board thickness and it carries out acid washing in a sulfuric-acid water solution 5%. The Zn-nickel system alloy plating was performed. Sb was added as antimony oxide (Sb₂O₃), using a sulfuric-acid acidity bath as a plating bath. In this way, the plating presentation of the obtained Zn-nickel system alloy-plating steel plate was investigated, and press-working-of-sheet-metal nature and corrosion resistance were evaluated. These were collectively shown in a table 1. The assessment approach of press-working-of-sheet-metal nature and corrosion resistance is shown below.

(1) The maximum punch load when performing a press-working-of-sheet-metal nature cupping test (a part for 25mm/in a contraction ratio 2.0, blank holder 0.5ton, and drawing rate) estimated. As a lubricating oil, the Idemitsu Kosan make Z-3 is used, and it is this to the front face of a Zn-nickel system alloy-plating steel plate 1 g/m² It applied.

Maximum punch load 4ton Following : O4 - 4.5ton : O4.5ton ** : The rust generating area when performing a salt spray test (JIS Z2371) for 336 hours with x(2) corrosion-resistance plating estimated. Less than 1% of rust generating area: O1 - 5%:O5% ** : In the x table 1, the examples 1-5 of this invention are contrasted with the examples 1, 2, and 3 of a comparison. Compared with the example 1 of a comparison by which Sb is not added during the plating bath, the examples 1-5 of this invention have good press-working-of-sheet-metal nature, and are equivalent. [of corrosion resistance]

[0012] However, if there is too much Sb under plating bath like the example 2 of a comparison, corrosion resistance will fall. Moreover, even if Sb of a suitable amount is added during the plating bath, when current density is too high like the example 3 of a comparison, there is no effectiveness in press-working-of-sheet-metal nature. The example 4 of a comparison and the examples 9-11 of this invention are contrasted with the example 5 of a comparison, respectively, the example of this invention has good press-working-of-sheet-metal nature compared with the example of a comparison by which Sb is not added during the plating bath, and the corrosion resistance of the examples 6-8 of this invention is also equivalent. The improvement effectiveness of the press-working-of-sheet-metal nature according [the examples 15-17 of this invention containing Co, little Fe, and little Cr and other examples of this invention] to Sb addition is clear, and corrosion resistance lowering is not accepted, either.

[0013]

[A table 1]

表1-1

区分	No.	めつき浴組成				pH	浴温(°C)
		Zn ²⁺ (g/l)	Ni ²⁺ (g/l)	Sb(ppm)	その他(g/l)		
本発明例	1	35	45	2		Na ⁺ 32	2 60
	2	35	45	1		Na ⁺ 32	1 60
	3	35	45	5		Na ⁺ 32	1.5 60
	4	35	45	3		Na ⁺ 32	3 60
	5	35	45	0.5		Na ⁺ 32	1.8 60
	6	30	30	3		NH ₄ ⁺ 14	2 60
	7	30	30	0.5		NH ₄ ⁺ 14	1.8 60
	8	30	30	1		NH ₄ ⁺ 14	1.5 60
	9	40	55	0.5		K ⁺ 22	2 50
	10	40	55	2		K ⁺ 22	1.8 50
比較例	11	40	55	1		K ⁺ 22	1.5 50
	12	45	60	2		Mg ²⁺ 10	2 50
	13	20	15	1		Mg ²⁺ 10	1.8 50
	14	60	80	1		Mg ²⁺ 10	1.5 50
	15	35	45	2	Co ²⁺ 10	Na ⁺ 16	2 60
	16	35	45	2	Fe ²⁺ 10	Na ⁺ 16	1.8 60
	17	35	45	2	Cr ³⁺ 5	Na ⁺ 16	1.5 60
	1	35	40	—		Na ⁺ 32	2 60
	2	35	40	7		Na ⁺ 32	1.5 60
	3	35	40	1		Na ⁺ 32	1 60
	4	30	25	—		NH ₄ ⁺ 14	2 50
	5	40	50	—		K ⁺ 22	2 50

[0014]
 [A table 2]

表1-2

区分	No	電流速度 (N/dm ²)	液流速 (m/min)	めっき組成		プレス 加工性	耐食性
				Ni (重量%)	その他 (重量%)		
本発明例	1	70	90	12		◎	◎
	2	150	90	11		○	◎
	3	50	90	10		◎	○
	4	10	90	13		◎	◎
	5	30	90	10		○	◎
	6	30	60	9		◎	○
	7	70	60	8		○	○
	8	100	60	9		◎	◎
	9	30	30	13		○	◎
	10	70	30	11		◎	◎
	11	100	30	12		◎	◎
	12	30	120	13		◎	◎
	13	70	120	10		◎	◎
	14	100	120	15		○	○
	15	30	90	12	Co 0.5	◎	◎
比較例	16	70	90	11	Fe 1	◎	◎
	17	100	90	12	Cr 0.1	◎	◎
	1	70	90	12		×	◎
	2	50	90	10		◎	×
	3	200	90	11		×	◎
	4	30	60	9		×	◎
	5	30	30	13		×	◎

[0015]

[Effect of the Invention] According to the manufacture approach of the Zn-nickel system alloy electroplating steel plate of this invention, maintaining the high corrosion resistance of Zn-nickel system alloy-plating original, it is possible to raise press-working-of-sheet-metal nature, and the suitable Zn-nickel system alloy electroplating steel plate for the automobile and household-electric-appliances application of which advanced press-working-of-sheet-metal nature is required can be offered.

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] Manufacture of a Zn-nickel system alloy electroplating steel plate is faced, and it is 0.5-5 ppm about Sb during a Zn-nickel system alloy-plating bath. It is made to contain and they are current density 10 - 150 A/dm². The manufacture approach of a Zn-nickel system alloy electroplating steel plate excellent in the workability characterized by electroplating to a steel plate.

[Translation done.]